<u>In Situ Thermal Treatment and Thermal Enhancement Technologies:</u> Notes on an Engineering Forum Roundtable Discussion

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INTRODUCTION

Moderators for the Roundtable discussion described the purpose for the Roundtable: 1) to bring together a group of experts on in situ thermal treatment and thermal enhancement technologies for a discussion on related issues; and 2) write a paper about these issues in order to help project managers and other technical personnel make knowledgeable decisions when considering the use of in situ thermal treatment technologies at their sites. The panelists included:

Roger Aines, Lawrence Livermore National Laboratory
Eva Davis, NRMRL-Ada
Craig Eaker, Southern Cal Edison
Raymond Kasevich, KAI Technologies, Inc.
Robin Newmark, Lawrence Livermore National Laboratory
John Reen, Terra Therm
Kent Udell, Berkeley Environmental Restoration Center

This Roundtable discussion is the third in a series of Roundtable discussions. Previous Roundtable topics were thermal desorption and permeable reactive walls.

PANELIST'S INTRODUCTORY COMMENTS

<u>In Situ Thermal Remediation</u>

A brief history of in situ thermal remediation was provided. Pre-1986, steam injection, electrical heating, radiofrequency heating (RFH), and in situ combustion were the primary thermal technologies, but almost all were used to reduce the viscosity of oil in preparation for oil recovery. In 1986, a pilot study using steam injection was conducted to enhance diesel recovery in the Netherlands, and in 1988, steam injection was used to enhance solvent recovery in the United States. In 1989, steam injection was used for diesel recovery at the Rainbow Disposal site in Huntington Beach, CA. In 1994, cyclic steam injection using dynamic underground stripping

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(DUS), electrical heating, and electrical resistance tomography (ERT) was used to remove gasoline at Lawrence Livermore National Laboratory (LLNL), and a six-phase electrical heating project to remove chlorinated solvents at Savannah River began. In 1995, cyclic steam injection was used at Naval Air Station (NAS) Lemoore, where a record 100,000 gallons of JP5 fuel was removed, and a steam injection project was initiated in Illinois to remove chlorinated solvents. In 1996, steam injection was used at Hill Air Force Base (AFB) to remove chlorinated solvents.

Lessons learned from the projects listed above were presented:

- Solvents vaporize in hot zones and migrate to colder zones where they condense;
- Downward migration of DNAPLs is a concern, but there is evidence that this now can be controlled;
- Vaporization of fluids (water and NAPL) can be caused by electrical or radiofrequency heating;
- Depressurization of the steam zone relaxes mass transfer constraints;
- Heating to 100^{o}C removes PCE and less volatile NAPL solvents;
- Thermal treatment does not eliminate microbial populations, especially fuel degrading ones;
- Monitoring of flow rates and subsurface temperatures is key to a project's success; and
- Definitive conclusions from pilot studies will be difficult to support because thermal technology pilot projects usually do not commit enough resources or time to prove success, especially in a generally contaminated environment.

Dynamic Underground Stripping

Dynamic Underground Stripping (DUS) is used to mobilize contaminants for removal and often is used in conjunction with hydrous pyrolysis oxidation (HPO). HPO is an in situ destruction process that occurs throughout, and even after, DUS. HPO is used as a "thermal polishing" technique that uses residual heat and available oxygen to destroy remaining contaminants. Bioremediation by indigenous thermophilic organisms also can play a role. Both DUS and HPO help drive ground-water contamination to MCLs. DUS can remove vadose zone contamination at approximately 15 times the rate of conventional methods, and ground-water contamination at greater than 60 times the conventional rate. Commercialization of DUS currently is being discussed. (Since the Roundtable, licenses for DUS have been issued to commercial vendors.)

DUS has been used at LLNL's gas pad site, where it was successful at removing free-product (mostly gasoline) and a "bathtub" ring of dissolved contaminants, even after pump-and-treat operations had proven unsuccessful. DUS also is being used at Southern Cal Edison's Visalia Pole Yard, where approximately 100,000 gallons of creosote from pole-treating operations have contaminated the site. A pump-and-treat system had been operating at the site for over twenty years with very low removal rates (10 pounds/week). In the first 6 weeks of DUSIHPO operation, about 300,000 pounds of contaminant were removed or destroyed. With DUS and HPO, the site is expected to close in 5 years instead of 30+ years with pump-and-treat—current bioremediation estimates indicate 120 years—at a cost savings of $30 M (net present value).

Dynamic Underground Stripping and Hydrous Pyrolysis Oxidation at Visalia Pole Yard

The DUS project to remediate DNAPL contamination at Visalia Pole Yard was discussed and a table explaining the site's history was presented:

1923-1980 Visalia Pole Yard Operated
1976 Ground-Water Pumping Initiated
1977 First Grout Wall Installation Completed
1985 Phase I Water Treatment Plant
1985 Cal-EPA Superfund Site
1987 Phase 2 Water Treatment Plant
1989 U.S. EPA Superfund Site Number 199
1992 Remedial Investigation/Feasibility Completed
1994 RAP/ROD
1995 Regulatory approval for DUS
1996 Design and Construction of DUS
1997 Remedial Action

A list of what was involved in the DUS process employed at the site was presented next:

- 200,000 lbs./hour steam produced by 11 injection wells
- Vapor extraction by 7 wells at 2,500 standard cubic feet per minute (SCFM) at approximately 20 in. mercury
- Vapor treatment/Thermal Oxidation
- Ground-Water Extraction at 400 gallons per minute
- Ground-Water Treatment—Separation, Filtration, and GAC
- Monitoring-ERT and Thermocouple
- Product recovery tracking

Wells were placed outside of the contaminant zone to heat the surrounding subsurface. This, in turn, caused the contaminants to migrate to the center of the plume where they could more easily be treated by DUS. Eaker noted that Visalia had 100% redundancy of its extraction wells and that each injection well could be individually measured for flow and pressure.

Hot Water Injection

Hot water injection was the first thermal technology used for oil recovery through viscosity reduction and is still used at some sites where other thermal technologies may not be successful. It is a “low tech” remedial option, but has application at sites where other thermal technologies cannot be applied. As an example, Davis cited a site in Virginia with a shallow water table and shallow contamination. The shallow conditions at this site make steam application unsafe, so hot water injection is being used as an alternative.

Radiofrequency Heating

One presenter’s first experience with RFH was at a site in Alaska where four antenna systems were installed at 15-foot depths to create temperatures of 20-30 ^{o}C below permafrost in order to bioremediate the site. After this installation, the presenter installed his first RFH system at a site in Utah. He used a 500,000 watt system at 13.56 megahertz to “retorque” oil shales located 500 feet below the subsurface.

RFH imparts heat to nonconducting materials through the application of carefully controlled radiofrequency transmissions. The technology can be used for controlled in situ heating of a variety of contaminants, thereby improving contaminant flow characteristics from subsurface soils. The technology can be applied using both vertical or horizontal boreholes in the area to be treated. A radiofrequency generator supplies energy through coaxial lines to multiple electromagnetically-coupled down-hole antennas. The temperature of the subsurface material between the antennas rises as it absorbs electromagnetic energy radiating from the antennas. Properly configured, the system provides a “steerable” heating pattern that can be controlled by varying the operating frequency, electrical phasings, and antenna length and position. RFH can heat soils to above 100^{o}C.

KAI Technologies used RFH to remove benzene from a capillary fringe. Applicators were placed at the capillary fringe and RFH was combined with SVE and sparging. The site was able to close at the conclusion of the remediation. A presenter indicated that he would like to do other remediations that combine RFH with other technologies.

KAI Technologies Company’s RFH units are leased and have been shipped all around the world for use at military and non-military sites. RFH is a cost-effective technology when applied at single-phase kilowatts; megawatt applications would not be cost effective. It is a low noise and low profile technology.

Thermal Wells and Thermal Blankets

Two of Terra Therm’s technologies were discussed: thermal wells, which are used at deep sites, and thermal blankets, which are used at shallow sites. Terra Therm, which is part of Shell Technology, Inc., has 25 years experience with heating the earth for oil recovery and uses capillary forces, heat flow, fluid flow, and modeling to better understand fluid flow in porous media. Terra Therm was founded on August 1, 1996, and currently is working at 72 sites in 5 states and Saipan. It is the single licensee for Shell’s patented in situ thermal desorption technologies and the commercialization agent for all existing and future Shell-developed environmental technologies.

Thermal wells are effective at remediating a variety of soil types, including clays, sand, and backfill, and work by evenly heating the subsurface. The highly uniform distribution of energy throughout the polluted region results in uniform treatment and complete removal of contaminants.

Thermal wells are 4-6 inches in diameter, and generally placed seven feet apart, but can be placed closer together at shallower sites. Usually, they are placed 14-20 feet deep and some (usually those placed in the center of the site) are installed with a vacuum. They can be used to treat difficult contaminants, such as PCBs, dioxins, and PAHs.

Terra Therm is not trying to compete with soil vapor extraction; rather it is trying to do rapid soil remediation. He added that Terra Therm is not trying to offer the “silver bullet” for all contamination, rather to go after the more difficult contaminants and provide quick cleanup timeframes.

QUESTION AND ANSWER SESSION

Contaminants That Can Be Addressed Using These Technologies

The panelists were asked which contaminants can be successfully remediated using thermal treatment. One panelist noted that some chemicals are easier to thermally treat than others. For example, steam injection can mobilize some metals but not others. He added that non-volatiles, especially PCBs, can vaporize, but the amount of steam needed is proportionate to the concentration of the contaminant. For example, low contaminant concentrations in soils may require only a modest amount of steam. More contaminated media require more steam and longer treatment times, increasing the cost of this technology.

Another panelist cited a report on steam stripping of industrial pollutants (Treatability of the Organic Priority Pollutants by Steam Stripping, Hwang, Seong T and Paul Fahrenthold (US EPA) AiChE Symposium Series: Water 1979, Vol 76 No 197, pp 37-60, 1980). This report examines what it takes to strip a priority list of pollutants from industrial effluent. The results indicate that low-volatility compounds (e.g., benzo-a-pyrene) may strip well in vapor form if dissolved in water. Only a few of the listed compounds do not strip readily. The panelist noted that he would consider targeting such compounds for in situ oxidation.

A panelist agreed that steam stripping is a powerful technique, but that it is not always successful on heavy metals. With heavy metals, a combination of technologies——such as electrokinetic technology in combination with thermal treatment——would work best. For example, the thermal treatment process could help increase soil permeability and contaminant mobility, and electrokinetics then could be used to move the ions through the soil to the electrodes. Another panelist noted that thermal wells have been successful at treating a “witch’s brew” of contaminants, as well as treating buried drums. As noted under Design Considerations below, in one instance, the end result was an exploded drum that caught on fire.

Impact of Ground-Water/Surface Water Discharge

In response to a question about whether thermal treatment can be applied in areas with ground water flow rates, a panelist noted that this should not be a problem. At Visalia, the ground-water flow rate is high, but steam injection has been successful. He then noted that soil has great heat capacity; once it is heated, it retains heat, even if even if there is influent cold water. Another panelist said that subsurface monitoring can be used to determine whether groundwater flow rates affect the success of a steam injection project by identifying “collapsed” heating fronts that can cause ground water to flow back into the heated area. She noted that field experiments have been conducted to determine dynamic fluid and hydraulic changes within a heated area and the effect these have on ground water outside the heated area. She then noted that high pressure gradients can change the natural gradient of a site during steam injection; the steam creates a barrier to fluid movement during injection. When steam injection is stopped, the subsurface temperatures will rebound to 100^{o}C at certain depths.

Downward Movement of DNAPLs

In response to a question about downward movement of DNAPLs in fractured bedrock, one panelist noted that RFH, when applied with SVE and air sparging, can control downward migration when the placement of the wells is optimal.

Design Considerations

Next, the panelists were asked about what they, as engineers, need to know to properly evaluate the design specifications of a thermal system. For example, what needs to be included in a design package, should pilot studies be conducted, and is soil characterization needed. With respect to steam, the volatilization of DNAPLs at lower temperatures permits greater control/recovery. The downward migration of a DNAPL has not been detected at Visalia.

One participant asked the Panel if they have ever used formation water for steam injection. A panelist said that he tried to use formation water at Visalia, but too much salt water accumulated in the system. Once they switched to municipal water, the problems ceased. He added that Visalia site managers had to spend a lot of money (17¢ a gallon) to move recovered softener waste off site. At one point during the operation, while they were operating at maximum capacity, they were hauling off three 6,000 gallon tankers a week of recovered waste. Luckily, municipal water was available for use at Visalia; in more remote areas this may not be an option.

Another panelist said that injecting softened water (water that has had its sodium replaced with calcium), can change clays slightly, but this change usually does not have a major affect. He added that no major clay mineralogy changes have been seen at the LLNL gas pad.

A participant asked whether the importance of abiotic and biotic components associated with in situ oxidation has ever been quantified, and to what extent in situ oxidation occurs in the soil. A panelist noted that hydrous pyrolysis oxidation occurs under the same conditions as bacterial degradation, and it is difficult to differentiate between them. However, since bacteria are known to not metabolize at temperatures above 100^{o}C, the CO2 that is produced in the subsurface at 100^{oC} or above is assumed to occur from chemical processes.

A participant then asked whether CO2 is found in the off-gas when using RFH. A panelist noted that no CO2 has been found at temperatures of 100-140^{o}C at Kirtland Air Force Base, which suggests that the biotic component is absent and the abiotic component is inactive. Another panelist noted that he would be surprised to see any abiotic component at a site where RFH is applied since RFH causes soils to dry out.

One participant asked whether thermal technologies can be applied at sites with buried drums. A panelist noted that, in his experience, there have been no problems with buried drums at sites where thermal blankets and thermal wells have been used; this is attributed to the way these technologies heat the ground. Another panelist said that a small underground drum that has rusted on the bottom and started to leak poses a great problem if heated, but other kinds of vapor tanks probably pose no problem.

Another panelist said that the rule of thumb for a DUS design is to surround the source with heat to push the contaminants toward the cluster of extraction wells. He added that it is important to make sure a guard well is in place to provide a “steam-bank” on the exterior of the contaminated area being targeted. In addition, steam should be injected from the bottom up. If volatiles are present, keep the area warm and under vacuum to control the movement of material being mobilized. Natural flow paths will take precedent; do not expect to change them. Monitoring will help tell you what is happening. Be sure your system has built-in flexibility to optimize contaminant recovery.

Another panelist said that any thermal method that uses electricity needs to be carefully engineered to deal with individual problems at sites, including those with buried drums. He added that drum sites are highly conductive and controlling current flow and radiation fields in them is more difficult. At high power, electrical heating could cause possible arching on the drums and create a hazard. Passive treatment using thermal blankets may be a better alternative.

One panelist said that she is aware of a report by Los Alamos on the application of electrical heating and RFH of a site that contained buried drums. At this site, the application of these two technologies caused the explosion of a buried drum and spread the drum's contaminants. She also said she was aware of a test conducted by Terra Therm where they filled a drum with ethanol, welded it shut, and electrically heated it. The end result was an exploded drum that caught on fire. From these two studies, she concluded that drums are a concern and cautioned about using electrical heating and RFH at sites where drums are present.

In response to a question as to whether it would be possible to maximize in situ oxidation in order to minimize contaminant extraction, one panelist said yes and noted that there may be instances where it is not desirable to bring contaminants to the surface. To do this with a DUS system, you would "huff and puff" the system slowly to allow for a large percentage of the contaminants to be destroyed in situ and not extracted. Another panelist indicated that there are rumors that dioxin can be formed with steam when chlorinated solvents are present, but this is not true. Another panelist noted that from what she has seen in the literature, it does not appear that the temperatures reached in steam processes are going to cause dioxin formation, not even from PCP, which is a precursor. However, the range of temperatures that can be reached using RFH and Terra Therm's in situ thermal desorber are within the range where dioxin formation can occur. She then noted that little research has been done to confirm that dioxin could be formed in situ, even with these technologies. In response to a question on DUS's near-surface applicability, one of the panelists noted that DUS is more effective at deeper depths where high temperatures can be more easily maintained. Deeper injection allows for higher temperatures and increased well spacing, which helps lower the costs. Shallower installations of DUS systems require a cover, which increases the costs. Another panelist noted that RFH is more cost effective if it is applied near the surface in conjunction with horizontal wells.

In response to a question about worker safety, a panelist noted that a group of industrial hygienists were sent to Visalia to measure air quality around the treatment facilities and in the areas where heat was found at the surface. Results of this investigation found that all contaminants were 1,000 times below the industrial limit. He warned, however, that good vacuum pumps still should be placed on the wells to ensure that all vapors get into the treatment system.

Another panelist presented the following design considerations for a DUS system:

- Individually design the wells for each site and be careful about where they are placed.
- There is no such thing as a "bullet proof" extraction pump.
- Be robust with the heat exchanger used at the site.
- The vacuum system only is limited by the largest pump that can be installed at a site.
- Don't use activated carbon for vapor phase treatment; it is too expensive.
- Track CO_2 and hydrocarbons in the condensable gases to optimize your system.
- The main expense when using a DUS system is water treatment; these costs can add up quickly.

Construction

In response to a question about whether RFH's performance is dependent on the frequencies it uses, a panelist noted that with RFH, you select only one frequency for the operation, which does not change throughout the entire operation.

In response to a question about the number of wells required during thermal well remediation, a panelist noted that the wells are placed seven feet apart both inside and outside the area of contamination. He added that the distance between wells is dependent on the depth and type of contamination.

One panelist said that DUS applies steam rapidly, so control is a major issue. Monitoring is crucial to understand how steam moves through the subsurface, and where to properly place the wells. In addition, it is important to build flexibility into your system so any well can be relocated easily if surprises are found.

Another panelist said that, in terms of site preparation, well placement for RFH is similar to well placement for SVE. RFH normally operates with a two-well system. The wells are fiberglass-lined and spaced 10-20 feet apart. Applicators are placed in these wells and operated at low power.

A panelist noted that the thermal wells and thermal blankets operate at 1.5-3.5 megawatts and is hooked up to a standard electrical grid. It is low profile, and creates no odor and low noise. The exclusion zone is small and there are many areas on the site where visitors can be safely brought onto the site. Continuous monitoring systems are used at the site. His company's thermal wells and thermal blankets use only standard equipment and are individually designed for each site.

One panelist suggested the following "shopping list" for steam projects:

- Multiple large tanks to store free-product,
- 1 tank for clean water,
- 1 condenser to get rid of the energy from the extracted fluids,
- 2 heat exchangers (1 for water-phase; 1 for vapor-phase),
- 1 separator,
- 1 vacuum system,
- 1 back-up generator to run the vacuum pumps during power outages to prevent vapor release,
- 1 steam generator fueled with diesel, propane, or natural gas,
- A surface covering for shallow sites without clays or another natural barrier, and
- A quench port for all wells, so that they can be "shut off" quickly with cold water, possibly from a garden hose

Present-Value Costs (Capital and Operation and Maintenance)

According to one panelist, Terra Therm estimates their thermal blanket and thermal well technology costs by the ton or cubic yard. Testing and sampling are separately costed-out because of the unknowns at any given site. Terra Therm's market price for its technologies is $100 per cubic yard, although they would prefer to target operating costs at $130-150 per cubic yard. The price for operations in dewatered areas goes up significantly to above $300 per cubic yard. To break this out further, 20% of the costs go toward power and the rest for mobilization and demobilization. Terra Therm prefers to work at large sites (3,000-4,000 cubic yards) but will work at sites as small as 1,000 cubic yards.

A panelist said that DUS costs can be separated into heating and treating process costs. At LLNL, the best way to determine costs was by volume of soil to be heated, rather than the amount of contaminants present. The energy costs at LLNL were very low because they used natural gas. Electrical applications are more expensive.

Another panelist said that RFH costs are separated in terms of temperature ranges. For example, low temperatures are used for bio-applicators, and higher temperatures are used when treating the vadose zone. A large scale bio-applicator project operates at 20-30^{o}C, which translates to a cost of $15-20 per cubic yard. Higher temperature operations (100-150^{o}C) will be more costly ($65-75 per cubic yard).

One panelist noted that EPA's SITE program published a report on steam injection at the Rainbow Disposal site that approximated cleanup costs at $35 per cubic yard for cleanup of 100,000 cubic yards of contaminated soil. However, if the boiler had been operated 100 percent of the time, these costs may have been reduced to $27 per cubic yard. At LLNL, cleanup costs are estimated to be $65 per cubic yard, which includes ERT, electrical heating, and personnel. For a larger site, the costs per cubic yard may be reduced because the engineering costs are not dependent on the size of the site. Engineering costs represent about 1/3 of the costs at LLNL.

One panelist noted that three different cost scenarios had been estimated for Visalia: $22M for ten years, $17M for five years, and $14M for two years. In each case these reflect 1-2 years of DUS treatment and 10, 5, or 2 years of post-DUS monitoring. These numbers do not include profit. The increase in costs for the different timeframes represents continuous monitoring, not the operation of boilers the entire time. Visalia spent $11M during its first two years of operation; $4M of that went toward hardware, $1.2M toward construction, $750,000 toward natural gas, and $300,000-400,000 toward treatment of hazardous waste on site. If the hazardous waste had been disposed off-site, the last cost would have increased to $1M. Visalia did not pay for the electricity used at the sites, but estimates indicate it would have cost $1M.

<u>Monitoring Requirements</u>

One panelist noted that basic monitoring for RFH is conducted with a computer program that can determine how efficiently the energy is heating the formation. Fiber optics are used to measure borehole temperature and temperatures in other parts of a well. When using RFH, OSHA standards for radiation emissions need to be met. To do this, measurements of radiofrequency levels around the borehole and at varying distances from the borehole are made.

A panelist noted that thermal well monitoring is conducted on each well with an array of temperature probes. It is controlled through a central computer system. Also, continuous emissions monitoring is conducted through a control system. Sampling usually is conducted by a third party.

A panelist noted that at Visalia, the effluent was monitored on a bi-weekly basis to make sure it met "nondetect" discharge requirements for PCP and creosote. A source test was conducted on the boiler to measure air quality, and performance-based monitoring was conducted on the activated carbon. No routine monitoring of the boiler was required. ERT was used to detect the “heat signatures” in the subsurface. After the project is completed, standard borehole monitoring will be required.

At the LLNL gas pad, a probe with an infrared sensor was used to continuously monitor the temperature distributions in the wells. The probe also was used during an RFH project at Kelly AFB.